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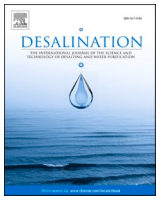

Water reuse and resource recovery from greenhouse wastewater by capacitive electrodialysis at pilot scale

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HIGHLIGHTS

- Pilot-scale CED is efficient for resource recovery from greenhouse wastewater.
- Irrigation water with conductivity <0.2 mS/cm and Na^+ < 0.1 mmol/L was achieved.
- Optimal operation at 12 V, 80 % recovery, 5.12 cm/s flow velocity and 2-stack staging.
- Nutrient showed concentration factors of K^+ (2.3), NO_3^- (2.7), and PO_4^{3-} (1.9).
- CED's energy consumption was 4-fold lower than RO.

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ABSTRACT

As food production dominates global freshwater consumption and nutrient discharge regulation tightens, the performance of novel technologies at applied scale needs to be studied to optimize water use and minimize environmental impact. Water reuse and the nutrient recovery from greenhouse wastewater were assessed utilizing one-pass capacitive electrodialysis (CED) at a pilot scale (19.32 m^2 membrane area, 1–4 m^3/day capacity), employing carbon-based electrodes. CED was optimized for key parameters, including applied voltage, cross-flow velocity, staging, water recovery, and varying feed concentrations. High-quality greenhouse irrigation water (conductivity<0.2 mS/cm and Na^+ < 0.1 mmol/L) was produced, meeting specified guidelines. Na^+ was retained less compared to Ca^{2+} and Mg^{2+} (86 % ± 4 %, 97 % ± 2 %, and 98 % ± 3 % removal, respectively) and nutrients concentration factors for K^+, NO_3^- and PO_4^{3-} reached up to 2.3 (596 ± 5 mg/L), 2.7 (1330 ± 20 mg/L), and 1.9 (130 ± 2 mg/L), respectively. There was no significant improvement in ion removal for all feed compositions beyond 12 V and 80 % water recovery. CED's specific energy consumption (SEC) with optimized parameters was 4-fold lower than the modeled RO system, and lower than previous electrodialysis studies. The highest SEC obtained was 0.24 kWh/m^3. These findings suggest that CED is a promising technology for the greenhouse horticulture sector, aiding the move toward zero liquid discharge.

1. Introduction

While 2 L of water would suffice as a daily drinking water requirement per person, it can take up to 3000 L to produce enough food and other crops to meet a person's daily needs [1]. Global freshwater consumption is dominated by agriculture at around 69 % [2], with agriculture not only consuming water resources but also polluting water bodies with fertilizers and pesticides. Greenhouse horticulture is an advanced solution that reduces the environmental impact of food production as it decreases water demand by up to 40 % as compared to open field cultivation [3], requires less area, produces higher yields, improves process control for crop production regardless of the local climatic

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conditions, and facilitates containment of pollutants [4]. In the Netherlands, greenhouse horticulture encompasses a relatively large area of about 10,000 ha, one of the highest in Europe [5]. In the Netherlands, the greenhouse industry has been at the forefront of integrating advanced technologies for water recirculation, aiming to reduce operational costs, water intake, and environmental footprint. However, the high yield of crops in this sector still necessitates significant resource input and results in considerable wastewater generation. This challenge is compounded by the impending legislative changes set to enforce stricter wastewater discharge standards by 2027 [6]. Additionally, the sector is increasingly contending with water scarcity, a consequence attributed to climate change impacts. This dual pressure from regulatory requirements and water availability constraints [7] has catalyzed the exploration of innovative solutions aimed at (near) zero liquid discharge (ZLD), to reduce greenhouse wastewater discharge further, optimize irrigation water reuse and resource recovery, in pursuit to meet the European Water Framework Directive (WFD) criteria.

Greenhouse wastewater can be treated at an individual grower level or collectively for several greenhouses. To close the water and nutrient loop at both levels, the wastewater generated is (i) treated to prevent the accumulation of undesired constituents such as sodium (Na^+) [8] and (ii) disinfected to prevent plant pathogen proliferation. Na^+ presents a notable challenge in greenhouse horticulture, as its presence is known to hinder plant growth. It is not actively absorbed by crops, leading to its accumulation in the water recycling system [9,10]. Existing literature outlines three primary standards that serve as benchmarks for repurposing water in greenhouse irrigation [11]. Additionally, through a series of interviews with greenhouse owners and representatives in the Dutch horticultural sector, a fourth criterion emerged, reflecting a more rigorous standard for water quality. Table 1 consolidates these findings, offering a comprehensive depiction of the targeted parameters investigated for the reuse of irrigation water in greenhouse horticulture.

Widely used membrane processes such as reverse osmosis (RO) have been extensively piloted and employed to treat greenhouse wastewater to produce consistent reusable water with low Na^+ concentrations [13–15]. RO can successfully remove ions from the wastewater to low concentrations ($Na^+ < 0.1$ mmol/L), for recirculation. However, all other ions including nutrients (K^+, NO_3^-, PO_4^{3-}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-) are also removed during the RO process, leading to higher osmotic pressure and necessitates the re-introduction of these nutrients into the re-circulating irrigation water. Consequently, this leads to an escalation in fertilizer use, which needs to be added to the source water to sustain crop growth, offsetting some benefits of RO treatment. Recently, electrically-driven membrane processes such as electrodialysis (ED) have emerged as promising alternatives to RO due to comparable, if not higher, energy efficiency and the potential of tunable ion removal to meet specific requirements for produced water [16]. Furthermore, ED is less sensitive to membrane fouling and can operate at a higher recovery rate of 90 % compared to 80 % for RO [17]. For applications similar to those in the greenhouse sector, the use of ED has been described in literature [18–24]. Additionally, recent developments in the fabrication of ion-selective membranes specifically for Na^+/K^+ separation have made ED an attractive solution for the enhanced valorization of nutrients [25–30].

Conventional ED processes use an electrode rinse solution (ERS) for converting electrical to ionic current through redox reactions or water splitting [31,32]. This ERS, however, adds system complexity due to a separate hydraulic circuit, risks generating harmful gases like Cl_2 and O_2, and cause electrode potential drop [33,34]. Capacitive Electrodialysis (CED) offers a solution by using capacitive electrodes, typically made from high surface area, conductive materials like activated carbon [34–36]. The carbon layer acts as a current collector where ionic current is converted into electric current through ion adsorption and desorption (holding/releasing electrons)-via porous capacitive electrodes, avoiding the production of harmful gases and eliminating the need for a separate ERS, thus simplifying operation and maintenance [37]. CED operates on the principle of an electrical double layer (EDL) forming to store ionic charges when electrical polarization is applied [38–40]. A limitation of CED is the potential saturation of the capacitive carbon layer, which is managed by periodically reversing electrode polarity to prevent charge build-up and mitigate fouling [31].

Thus, overall, CED has the potential to exhibit up to 3-fold more energy efficiency compared to RO and other conventional technologies, and can be more effectively coupled with renewable energy sources (e.g., solar or wind energy), thus facilitating a substantial reduction in carbon emissions [41,42]. Moreover, CED's advanced operational efficiency is highlighted by its ability to achieve water recovery rates of up to 90 % [17], significantly minimizing the volume of wastewater requiring disposal. Furthermore, a distinct advantage of CED lies in its potential for targeted nutrient retention and recovery, thus reducing the demand for synthetic fertilizers as well as enhancing the sustainability of agricultural practices [20,25]. Additionally, the process benefits from a reduction in chemical usage as it circumvents the need for ERS [37], and in fouling mitigation requirements (e.g. cleaning, maintenance, chemicals usage), due to its inherent property of electrode reversal [31]. It is an innovative and sustainable solution for simultaneous high-water recovery and ion concentration (e.g., nutrients) at low energy and chemical consumption from feeds such as greenhouse wastewater. Promising results for desalination, irrigation water reuse, nutrient recovery and energy efficiency have been achieved with C (ED) at lab-scale [18,20,22,43] and applied scale [21,44,45]. For application in the greenhouse horticulture sector, however, to the best of the authors' knowledge, this is the first time CED has been investigated with a capacitive electrode-based system, specifically, at pilot scale, a missing step toward the full-scale implementation for resource recovery in the greenhouse horticulture sector.

This study investigated the feasibility of a pilot-scale CED system (1–4 m^3/d), utilizing capacitive electrodes to meet the target irrigation water requirement and assess the nutrient concentration potential from greenhouse wastewater. Short-term CED experiments in one-pass mode were conducted to: (i) evaluate optimal operating parameters, including applied voltage, cross-flow velocity, stack staging, and varying feed concentrations (for individual and collective greenhouses), to produce diluate streams that aligns with greenhouse irrigation water quality standards, (ii) analyze the impact of operating parameters on diluate quality and ion transport (specifically for Na^+), and (iii) assess the composition and nutrient recovery potential of the concentrate generated. Furthermore, (iv) specific energy consumption (SEC) of the CED system was determined and compared with conventional ED and (modeled) RO performance.

Table 1
Conductivity, Na^+, and Cl^- guidelines for greenhouse horticulture irrigation water.

S. no.	EC (mS/cm at 25 °C)	Na^+ (mmol/l)	Na^+ (mg/l)	Cl^- (mmol/l)	Cl^- (mg/l)	Ref.
1	<0.2	<0.1	<2.3	<0.1	<3.5	[12]
2	<0.5	<1.5	<35	<1.5	<53	[11]
3	0.5–1	1.5–3	35–69	1.5–3	53–107	[11]
4	1–1.5	3–4.5	69–104	3–4.5	107–160	[11]

2. Experimental methods

2.1. Feed water compositions

Three feed water compositions were assessed: synthetic greenhouse wastewater mimicking the composition of individual (IGW) and collective greenhouses (CGW) and real greenhouse wastewater (RCGW) obtained from a collective greenhouse treatment facility (60 greenhouses) in the Netherlands. The synthetic wastewater was prepared using KH_2PO_4, $NaHCO_3$, NH_4HCO_3, $NaNO_3$, $MgSO_4$, KNO_3, and $CaCl_2$

obtained from Merck Nederland (99 %). Table 2 provides the compositions for the three greenhouse wastewater feeds. The concentration of micronutrients (e.g., Fe, Mn, Zn, B, Cu, and Mo) was neglected in the synthetic wastewater as they were a minor constituent of the composition.

2.2. Capacitive electrodialysis (CED) pilot and operation

The CED pilot configuration is shown in Fig. 1 (FUJIFILM Europe B. V.). This set-up consisted of 2 membrane stacks with 4 hydraulic stages and 150 ion exchange membrane pairs (19.32 m^2 effective membrane area), with a alternating cation– and anion-exchange membranes (CEMs and AEMs Type 10, FUJIFILM Europe B.V.). The electrode area per-sheet was 400 cm^2, and the thickness of the spacers was 270 μm (Deukum GmbH) producing separate diluate and concentrate channels. Activated carbon-based coated anode and cathode electrodes were used with CEMs as end membranes in direct contact (3 mm thickness). The detailed process diagram, specifications, and images of the set-up and membranes are provided in the supplementary information. The characterization of capacitive electrodes was out of scope for this study. The voltage (V), current (A), pressure drop (bar), electric conductivity (mS/cm), cross-flow velocity (cm/s), and pH of the feed, concentrate, and diluate were logged every 5 s with a datalogger (Midi Data Logger GL840, Graphtec).

The linear cross-flow velocities of the feed, diluate and concentrate were monitored with diaphragm pumps (CF-20, Fuan Bidibao) controlled by built-in cross-flow meters (SC 100 AS, Altometer). All membranes in the stack were equilibrated for 1 h with feed water without applying voltage before each experiment to condition the membranes to the feed water. Potentiostatic conditions (constant potential, V) were maintained for all experimental conditions with a power supply (PPS-11815, Voltcraft), and the current (mA) was recorded for all runs. The CED pilot was operated in one-pass mode (Fig. 1). First, the feed water (Q_f) was pumped to stack 1 from the feed tank (100*L*). Then, the outflow from stack one was directed to stack 2. Finally, the generated diluate (Q_d) and concentrate (Q_f) were collected separately, as irrigation water and concentrate (alternatively). The CED set-up was operated in 2 cyclic modes; a charged mode, where cations and anions passed through the CEMs and AEMs, adsorbing in the cathode and anode respectively (Fig. S1.b). After a fixed time period (~10 min), the system was operated in a discharge mode, by switching the electrode polarity (~2 min) coupled with exchanging the diluate and concentrate outflow channels. This switch resulted in the movement of ions being reversed i.e. the desorption of cation and anions from the cathode and anode respectively (Fig. S1.b). The charging and discharging mode were alternated periodically, after the fixed time mentioned before to limit the saturation of ions on the capacitive electrodes (capacitive electrode regeneration), in order to avoid zero current flow (no ionic movement) [33,39,46].

2.3. Experiments, sampling and calculations

The CED performance was investigated over a range of operating parameters for all the greenhouse wastewater feed compositions. Table 3 shows an overview of the experimental conditions tested, with the target to achieve diluate conductivity below the set-points (Table 1). All experiments were conducted for 1 h and the feed water tank refilled once empty. All experiments were conducted in duplicates for statistical significance. Samples for feed, dilute, and concentrate analysis were collected and analyzed to determine the diluate ion composition, ion transport, energy consumption, and concentrate composition. Ion concentrations were analyzed by ion chromatography (930 compact IC flex, Metrohm) and total organic carbon (TOC) and inorganic carbon were determined using a TOC analyzer (TCO L-series, Shimadzu). Furthermore, scaling was estimated using the software Membrane Master (Genesys International). The relevant equations and calculations for the operating parameters, including cross-flow velocity, water recovery, ion transport number, relative transport number, and water transport, and the performance parameters: ion removal, concentration factors, and specific energy consumption (stack and pump) are provided in the supplementary information.

2.4. Reverse Osmosis (RO) model

The performance of reverse osmosis (RO) for greenhouse wastewater treatment was simulated using the WAVE software (version 1.82, Dupont) to assess its performance compared to CED. Compositions similar to RGW feed were used in the modeling with total dissolved solids (TDS) concentration of 1377 mg/L and EC of 2.16 mS/cm. The configurations used in the model as a function of the number of elements per stage, the initial recovery, and water recirculation are provided in the supplementary information. From the model, the specific energy consumption (SEC) per m^3 of permeate of the RO system and the composition of the permeate and concentrate produced were calculated and compared to the results from the CED experiments.

3. Results and discussion

First, variations in operating conditions for capacitive electrodialysis CED are performed to determine optimal process conditions to obtain highest diluate water quality, nutrient concentration and energy efficiency. Second, the diluate water quality for reuse as irrigation water and the composition of nutrients in the concentrate for recovery are assessed. Finally, the (model) RO results are compared with experimental results from the CED pilot.

3.1. Operating parameters

The CED efficiency was assessed with an emphasis on producing irrigation water from greenhouse wastewater. Operation and design parameters investigated include applied voltage, water recovery, cross-flow velocities, staging, and varying feed concentrations.

3.1.1. Effect of applied voltage and water recovery

In the CED process, applied voltage is an important parameter that drives ion transport, determines desalination efficiency, and energy consumption. While higher voltages enhance ion flux, they also increase energy consumption [17]. Water recovery (WR) represents the proportion of diluate produced from the total feed water volume. Increasing WR reduces pre-treatment and pumping costs, as well as the volume and disposal costs of concentrate or brine [47]. However, higher WRs can lead to increased energy consumption and variable membrane area requirements. Thus, the effect of increasing applied voltage (0–16 V, 0.15–0.64 A) and water recovery (60–90 %) was investigated to

Table 2
Synthetic and real greenhouse wastewater feed compositions investigated in this study.

Parameter	Abb.	EC	pH	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^-	PO_4^{3-}	Ref.
Units		*mS/cm*		*mmol/L*										
Synthetic collective greenhouse wastewater	CGW	1.7	7.2	0.80	2.30	7.73	3.05	1.31	3.80	7.82	0.42	5.99	1.02	[12]
Synthetic individual greenhouse wastewater	IGW	2.5	7.9	0.62	6.50	7.05	8	3.5	11	8.76	6	6.10	0.7	[11]
Real collective greenhouse wastewater	RCGW	1.9	8.2	0	2.3	8.41	3.38	1.74	5.00	9.10	0.20	6.23	1.36	[12]

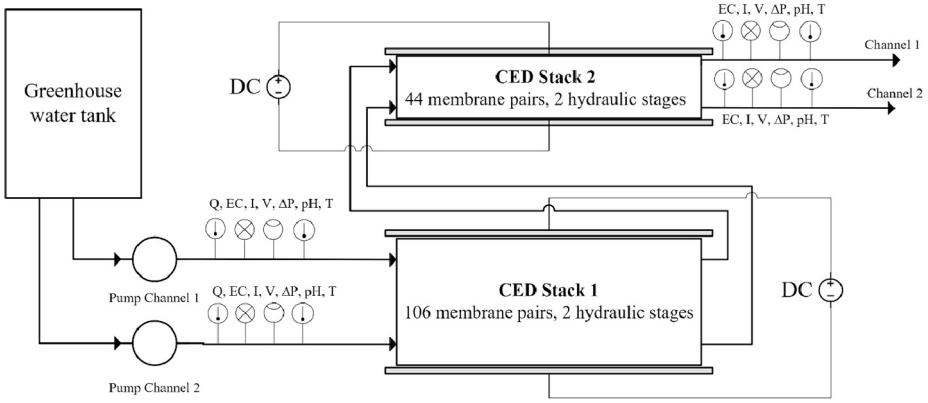

Fig. 1. Schematic of the capacitive electrodialysis (CED) pilot.

Table 3
Overview of experiments and operating parameters.

Experiment	Feed	Feed EC (mS/cm)	Diluate EC target (mS/cm)	Operating parameters
Control	NaCl synthetic feed	9	1, 0.5, 0.2, <0.2	For standardization, voltage variable, water recovery 50 %
1	CGW	1.7	1, 0.5, 0.2, <0.2	Cross-flow velocity 5.12 cm/s, stack staging 2-stages, voltage 6-16 V, water recovery 60 %, 80 % 90 %
2	IGW	2.5	1, 0.5, 0.2, <0.2	Cross-flow velocity 5.12 cm/s, stack staging 2-stages, voltage 6-16 V, water recovery 60 %, 80 % 90 %
3	RCGW	1,9	1, 0.5, 0.2, <0.2	Cross-flow velocity 5.12 cm/s, stack staging 2-stages, voltage 6-16 V, water recovery 60 %, 80 % 90 %

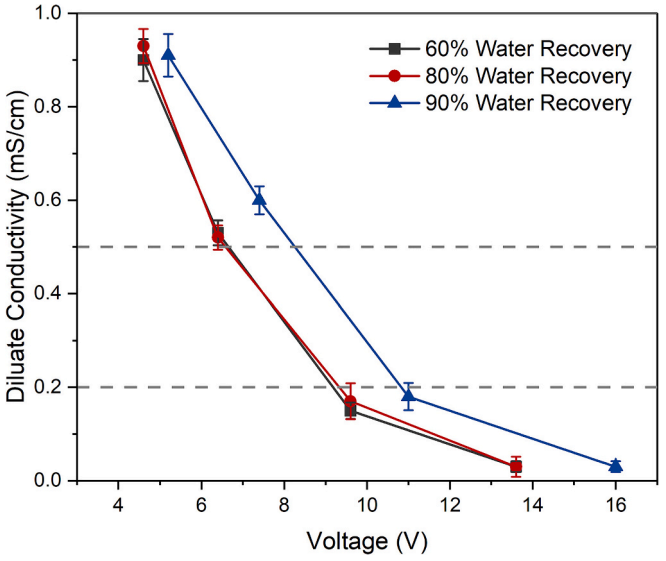

Fig. 2. Diluate conductivity (irrigation water quality) reached by the CED stack with the CGW feed composition (conductivity 1.7 mS/cm), 2-stage stack and cross-flow velocity 5.12 cm/s. The dashed lines represent conductivities of 1, 0.5 mS/cm and <0.2 mS/cm as target irrigation water quality (Table 1).

optimize the CED process, operated in one-pass mode, fed with greenhouse wastewater (CGW, IGW and RCGW). Fig. 2 depicts the ion removal performance of the CED stack with the CGW, representing the general trend for all 3 feed compositions. For CGW, increasing the voltage from 4 V to 16 V improved ion removal, lowering ion concentrations in the diluate from 1 mS/cm to <0.2 mS/cm (Table 2). The maximal voltage of 16.3 V was recorded for IGW at 90 % WR. For the highest target irrigation water quality (conductivity <0.2 mS/cm, Table 2), the system equilibrates between 10 and 16 V, with conductivity reduction plateauing at around 10 V, regardless of WR (slope decreases from 9.50 at 6–8 V to 1.75 at 10–16 V). Here, the effect of concentration polarization and stack resistance (increasing concentration difference) with an increase in voltage would start taking effect, decreasing the system efficiency [17].

A positive correlation was observed between ion removal and voltage, and higher WRs required more voltage to achieve equivalent ion removal. Similar results have been reported for other C(ED) studies [21,39,48]. Unlike the conventional one-pass ED process that uses an electrode rinse solution (ERS) where an optimum operation is determined based on the limiting current density [49], CED employs activated carbon electrodes. Therefore, ion removal at higher voltages is attributed to enhanced electrode polarization and electric double layer (EDL) compression at the electrodes while charging, which increases the electro-absorption area [50]. Hou et al. [51] investigated the mechanism of electro-adsorption of NaCl on activated carbon electrodes for capacitive deionization (CDI) and demonstrated an increasing correlation between voltage and solution concentration on EDL capacitance and electro-adsorption capacity. Literature studies have shown the importance of electrostatic and affinity effects [52] and the influence of charge and hydrated radius [43] for ion adsorption in mono-ion solutions at low voltages of 1.2 V. Li et al. [53] demonstrated that the hydration ratio determined the electro-adsorption capacity of ions on activated carbon electrodes for multi-ion solution for CDI also at 1.2 V. Other studies have reported a positive effect of voltage increase on ion removal [45,54]. Additionally, water transport was also evaluated to understand its effect on current loss efficiency, with minimal impact observed, although deviations increased from 2 % at 60 % WR to 5 % at 90 % WR (supplementary information). This variation is likely due to osmotic pressure and electro-osmosis effects, where water molecules are transported over the IEM membrane with their ion hydration shell [55,56]. This study provides initial insights into the voltage and water recovery effects on ion removal and electrode performance for CED with multi-ion solutions, informing potential full-scale CED applications in greenhouse wastewater treatment.

3.1.2. Effect of cross-flow velocity and stack staging

Cross-flow velocities (CFV) and stack staging are important parameters for pilot CED performance optimization. Based on indstrial

standards, velocities of 5.12 cm/s and 7.72 cm/s were investigated for ion removal, with CGW as feed composition [17]. An increasing relationship between voltage and conductivity removal was observed for both CFV rates (Fig. 3a), though diminishing returns became evident at higher voltages, particularly beyond 10 V. CFV can influence ion removal in 2 ways: i) higher CFVs (creating turbulance) can decrease the thickness of the diffusion boundary layer, causing faster ion removal, and ii) by reducing the resident time in the stack, thus decreasing the ion removal rate [32]. In this study, the 5.12 cm/s CFV runs, with around 30 % longer residence time, allowed for more prolonged ion interaction within the CED system at a given voltage compared to the 7.72 cm/s runs. Consequently, higher voltages were required to achieve similar TDS removal at the higher CFV. Previous studies further support the notion that residence time significantly influences process efficiency more than boundary layer mixing [57]. Other studies also observed a negative correlation between increasing CFV and salinity removal [58,59]; however, some studies have reported positive effects for batch electrodialysis reversal (EDR) systems [60].

Additionally, the CED performance under two configurations was assessed: a 1-stage setup with 106 membrane pairs (13.65 m^2 membrane area) and a 2-stage setup with 150 membrane pairs (19.32 m^2 membrane area), both operated in co-current mode. Fig. 3b compares these configurations for ion removal across 6-12 V. Both setups showed an inverse correlation between voltage and diluate conductivity, indicating enhanced effectiveness at higher voltages. However, the 2-stage arrangement proved more efficient than the 1-stage setup for ion removal, particularly at increased voltages in one-pass mode, to achieve all target diluate conductivities as per the irrigation water quality guidelines (Table 1). Similar to CFV findings, diminishing returns with voltage elevation were observed, more so in the 1-stage setup. This trend remained consistent across tested water recoveries. Therefore, for achieving the highest diluate quality (conductivity<0.2 mS/cm), further experiments were conducted using the 2-stage configuration with a CFV of 5.12 cm/s.

3.1.3. *Effect of varying feed concentration from greenhouse wastewater*

With the previous determined CED process conditions (section 3.1.2), the ion removal performance for the three feed compositions CGW (1.7 mS/cm), IGW (2.5 mS/cm), and RCGW (1.9 mS/cm) was evaluated (Fig. 4). IGW showed the highest removal across the range of voltages, suggesting that higher initial feed TDS results in higher ion removal efficiency. CGW follows closely behind, and RCGW has the lowest ion removal performance. This may be attributed to additional constituents present in RCGW such as suspended solids or charged organic molecules that negatively impact removal efficiency. These constituents are also removed relatively slowly and occupy charged sites in the membranes, slowing down the efficiency of desalination processes [61,62]. In CED, more ions are transported across the ion exchange membrane at higher feed concentrations; however, this is at the expense of a higher driving force, thus increasing energy consumption. With more salt removal, there is an increase in counterion flux, causing sharper concentration gradients and back diffusion, leading to a more inefficient system. Patel, Biesheuvel and Elimelech [41] showed a decline in current efficiency for increasing ion removal for feed concentration from 3 g/L TDS. The maximum feed concentrations for this study were significantly below 3 g/L, varying from 1200 and 2000 mg/L, providing a suitable and efficient case for CED application, over the range of feed compositions investigated.

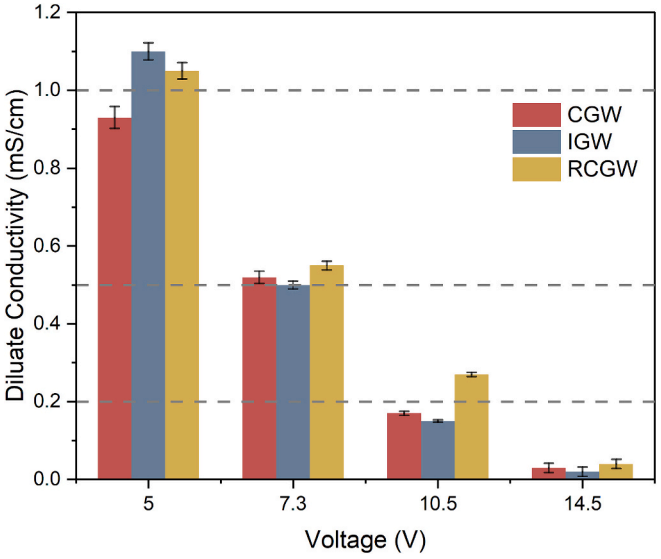

Fig. 4. Effect of varying feed composition (CGW, IGW, RCGW) on ion removal with increasing voltage at 90 % water recovery. The dashed lines represent target irrigation water conductivity 1 mS/cm, 0.5 mS/cm and < 0.2 mS/cm respectively, (Table 1).

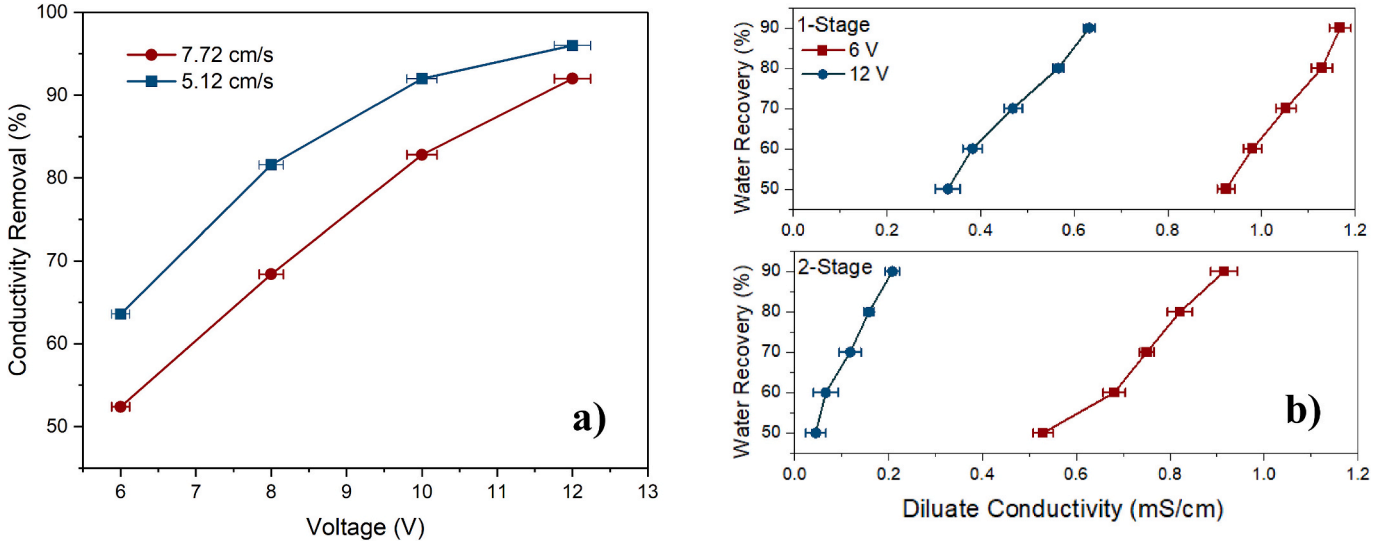

Fig. 3. Comparison of a) cross-flow velocities between 5.12 cm/s and 7.72 cm/s and b) 1-stage and 2-stage stack arrangement with CGW feed composition (conductivity 1.7 mS/cm).

3.2. Diluate water quality

The composition of the generated diluate (product water) was assessed, as it is important, especially for fit-for-use applications such as greenhouse horticulture, to reduced certain ions to specific levels. All three feed compositions reached the highest-quality greenhouse irrigation water (conductivity <0.2 mS/, Na^+, and Cl^- < 0.1 mmol/L - Table 2). Fig. 5 illustrates all the ion removal trends to attain target irrigation water conductivities for CGW at 60 % and 90 % water recoveries, representing the general trend for the 3 feed compositions.

Monovalent ions, specifically cations, with small ionic radii (e.g., Na^+, K^+) remained in relatively higher concentrations in the diluate as compared to other ions, even at lower diluate conductivity levels of <0.2 mS/cm. In general, K^+ declined more steadily across the diluate range than Na^+, Ca^{2+} and Mg^{2+} show a steeper decline in concentration, becoming almost negligible below <0.2 mS/cm. NH_4^+ has a significantly low or negligible feed concentration and is removed below detection limits across all dilutions. The Na^+ concentration in diluate declined sharply from 178 mg/L in the feed to 4.6 mg/L at 60 % water recovery and became negligible below <0.2 mS/cm, from 80 % water recovery onwards. Anion removal trends were more consistent across water recoveries for all feed compositions. Chloride (Cl^-) decreased from 277 mg/L in the feed to 3.3 mg/L at 60 % water recovery and fell to <0.1 mg/L for 80 % water recovery. For RCGW at 60 % water recovery, the ion concentration over the diluate range shows a similar but higher trend than CGW. This can be a consequence due to the presence of particulate or organic substances, e.g., the average TOC content of the RCGW feed was 9 ± 3 mg/L (compared to 0 mg/L for CGW), which could have impacted the ion removal performance. TOC generally consists of negatively charged compounds (e.g., organic acids etc.) that can potentially inhibit anion removal due to competition, or due to similar or smaller size than the membrane free volume, thus, transporting through the membranes [63].

In general, the ion removal percentage for cations followed the trend $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ and for anions $PO_4^{3-} > SO_4^{2-} > NO_3^- \sim Cl^- > HCO_3^-$ (Fig. 6, CGW at 80 % water recovery). These trends can result from several factors, including the effect of initial ion concentration, ionic size and charge, and competitive ion exchange on the membrane and capacitive electrode [17]. For runs targeting diluate conductivity of 1 and 0.5 mS/cm, Ca^{2+}, and Mg^{2+} reached above 95 % and 85 % ion removal, while Na^+ and K^+ were only removed by 42 % and 60 %, respectively. Whereas for target diluate conductivity of 0.2 and < 0.2 mS/cm, Ca^{2+} and Mg^{2+} reached above 97 % ion removal, while Na^+ and K^+ were removed upto 86 % and 95 %, respectively. This can be explained as in a capacitive system, with multivalent cations present, the sorption coefficients of divalent ions can potentially be higher than monovalent ions due to a reduction of the Donnan potential (higher ionic charge), enhancing their affinity, in proportion to bulk ion concentrations [43,64–66]. Furthermore, the selective preference of divalent over monovalent ions dominates at low current densities, where the effect of the affinity of sulfonic groups to the CEMs impacts the ion transport [67–69]. As current density increases, the boundary layer concentration gradient steepens, and the monovalent ion transport through the boundary layer is enhanced due to the higher diffusivity of monovalent cations over divalent cations [70], in additon to higher salt removal due to an increase in applied voltage. Xu et al. [44] have previously observed a dominant flux of Ca^{2+} over Na^+ and a selective transport of Mg^{2+} over Na^+ for treating municipal wastewater with a pilot-scale ED reversal (EDR) system. They also recorded an enhanced flux for SO_4^{2-} over Cl^-, attributed to the higher electrostatic attraction of negatively charged sulfonic groups with double-charged divalent ions in the electric field.

The overall selective transport of divalent over monovalent ions was confirmed by the relative transport number (RTN) values, given as the normalize transport number of divalent ions versus the average monovalent ion (Na^+) transport, which decreased with increasing water recovery and applied voltage, stabilizing around <0.2 mS/cm. Fig. 7 presents the RTN for divalent ions with CGW at 80 % water recovery, and additional data is provided in the supplementary information. The RTN of the diavelt ions was obsered to be 1.5–2 times the RTN of monovalent ions. Furthermore, Mg^{2+} shows lower RTN than Ca^{2+}, more so at lower current densities. This is attributed to Mg^{2+} having a larger hydrated energy (1921 kJ/mol) than Ca^{2+} (1577 kJ/mol) as well as lower diffusivity (7.05 × 10–10 m/s) than Ca^{2+} (7.93 × 10–10 m2/s) [71–73].

3.3. Analysis of concentrate and fate of nutrients

In addition to desalinating the diluate for water reuse, the CED system was examined for it's capability to concentrate ions for nutrient recovery from greenhouse wastewater. As demonstrated in Figs. 8 and 9, at a water recovery rate of 90 %, both cations and anions in CGW and IGW feeds exhibited higher concentration levels.

Notably, the concentration factors followed the order of $Ca^{2+} > Mg^{2+} > K^+ \sim Na^+$ for cations and $SO_4^{2-} > NO_3^- \sim Cl^- > HCO_3^- > PO_4^{3-}$ for anions. This trend suggests a greater affinity for concentrating divalent over monovalent ions at lower voltages, corroborating findings from diluate quality analysis (Section 3.2). However, the concentration

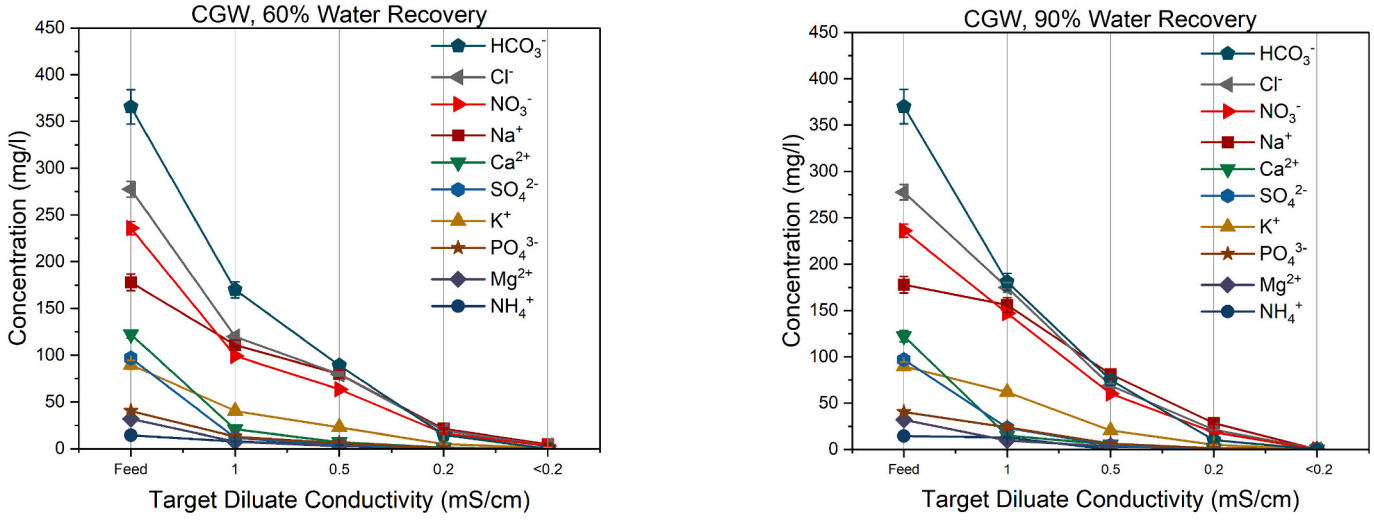

Fig. 5. Cation and anion removal from CGW at 60 % and 90 % water recoveries.

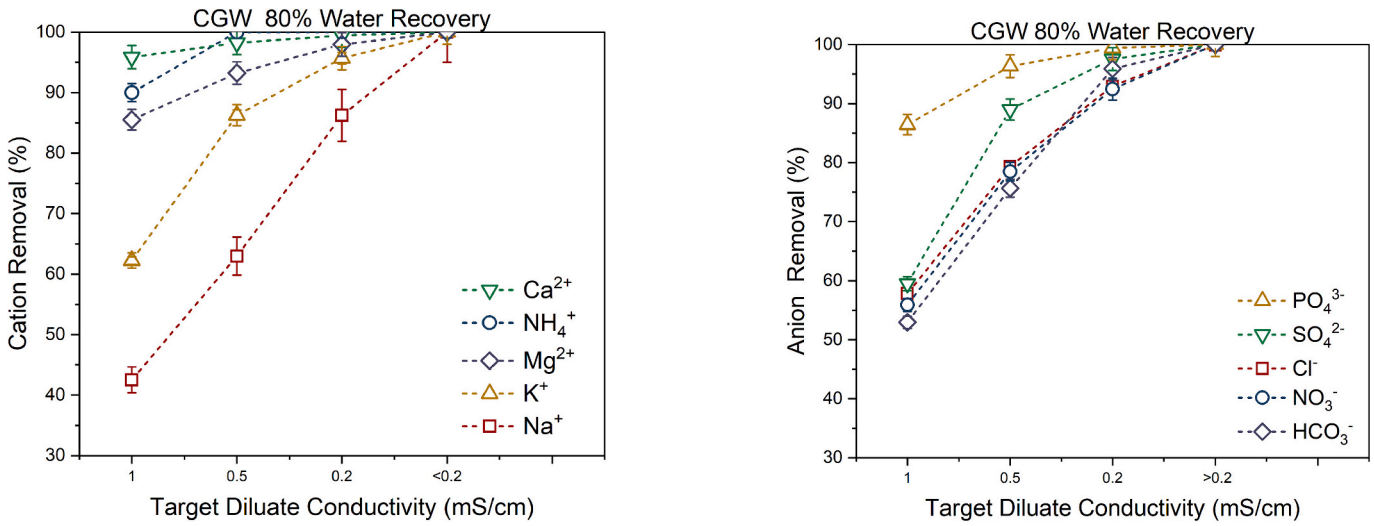

Fig. 6. Cation and anion removal percentage for CGW at 80 % water recovery.

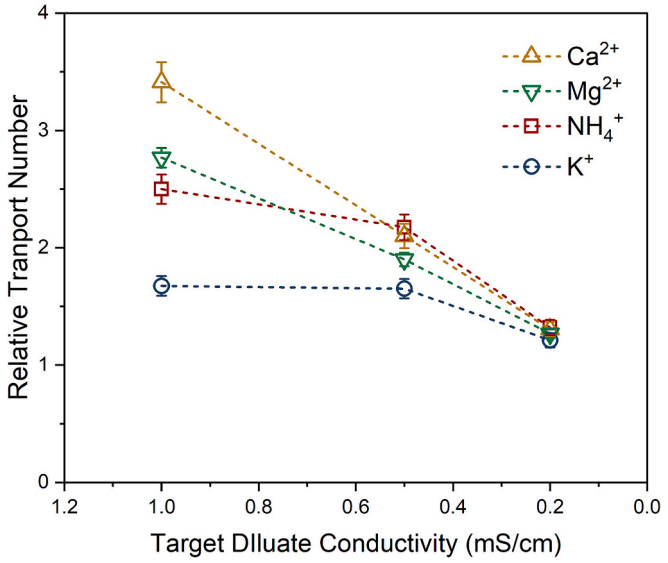

Fig. 7. Relative tranport number (RTN) values for the divalent ions with Na^+ as standard ion for CWG, at 90 % water recovery.

factor for PO_4^{3-} was lower due to its initial low feed concentration. Higher initial feed compositions, IGW (2.5 mS/cm), led to increased concentration factors, although this effect plateaued around 80 %, potentially due to co-ion transport or back-diffusion due to the concentrate gradient between the diluate and concentrate streams. Furthermore, it was observed that while high water recoveries enhance ion concentration, they also lead to reduced removal efficiencies, a trend previously observed in conventional ED with back diffusion [74,75] and uphill transport due to the transport of divalent ions from low to high concentration side of the membrane [76] being the limiting factors. The concentrate from the CED experiments showed potential for multi-ionic nutrient recovery, particularly for ions such as K^+(2.4, 2.3), Ca^{2+}(4.6, 4.1), Mg^{2+}(3.8, 3.6), NO_3^-(2.7, 2.1), HCO_3^-(2.5, 2.3), and SO_4^{2-}(1, 1.9), 90 % water recoveries for CGW and IGW respectively (Fig. 8). However, selective removal of undesirable ions such as Na^+ and Cl^- is necessary for optimizing recovery. Previously, studies have reported concentration factors for mainly one nutrient recovery. Mandor et al. [77] reported a K^+ concentration factor of 3.8 from swine manure. Rotta et al. [22] reported a concentration of $H_xPO_4^{3-x}$ up to 0.120 g/L and concentration factors of Na^+, SO_4^{2-} and $H_xPO_4^{3-x}$ higher than 9.7 from low phosphate-containing municipal wastewater feed (0.015 g/L of $H_xPO_4^{3-x}$). Ward et al. [21] demonstrated NH_4-N concentration by ED of 7100 ± 800 mg/L with a concentration factor of 8 from municipal wastewater. The results from this study are one of the first to provide new insights into the nutrient composition in the CED concentrate for extraction, aiding the selection and development of concentrate treatment technologies and strategies for achieving legislative targets regarding zero emission greenhouse wastewater discharge standards by 2027 [6].

To further optimized multi-ionic nutrient recovery, applying monovalent-selective membranes with divalent over monovalent selectivity can be a solution, however, it entails higher energy cost and lower ion fluxes [78,79]. Ahdab et al. [20] investigated the monovalent selective membranes at lab-scale which selectively separate Na^+ and retain divalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-}) in the diluate, with the membrane perm-selectivity performance of 1.6–3.2 removal of Na^+ and 1.9–3.6 removal of K^+ relative to Ca^{2+}. Complete optimization for nutrient recovery could ideally be achieved by developing Na^+/K^+ ion-selective membranes to separate Na^+ from the matrix while retaining K^+, a challenging separation due to identical ionic properties. Recently, novel studies have demonstrated reaching up to Na^+/K^+ selectivity of 1.8 with hot-pressed PSS-PVA saloplastics and 6 with supported liquid membranes [25,26]. However, these membranes are currently only tested at lab-scale and are yet to be validated for up scalability and their techno-economic feasibility at applied scales. Hybrid combinations with electrochemical processes such as CED (e.g. in combination with ion-exchange, Donnan dialysis, etc.) are currently promising to further maximize the valorization of resources [80,81].

Furthermore, this study addressed the challenges of scaling in electrochemical membrane processes, particularly due the presence of inorganic species, such as Ca^{2+}, SO_4^{2-}, and CO_3^{2-}, at higher concentration [17,82]. High water recoveries of 90 % for all feed water compositions, resulted in the maximum scaling potentials for $CaCO_3$, $CaSO_4$, and Ca_2PO_4, were 156.42 %, 45 % and 79,54 % saturation, respectively, based on simulations (Membrane Master Software, Genesys International, USA). The CED process, employing periodic polarity reversals every 12 min, potentially effectively mitigated inorganic scaling, as evidenced by the absence of significant scaling on membranes and spacers, based on observation post-experimentation. Further analysis of the membrane (perm-selectivity, water permeability and electrical resistance) and spacer (SEM-EDX and FTIR) should be done to validate the impact of scaling, post long-term operation. While current reversal is a recognized strategy to reduce scaling and fouling in industrial ED processes, reducing the frequency of membrane cleaning [83], it's essential to conduct long-term pilot studies with greenhouse wastewater

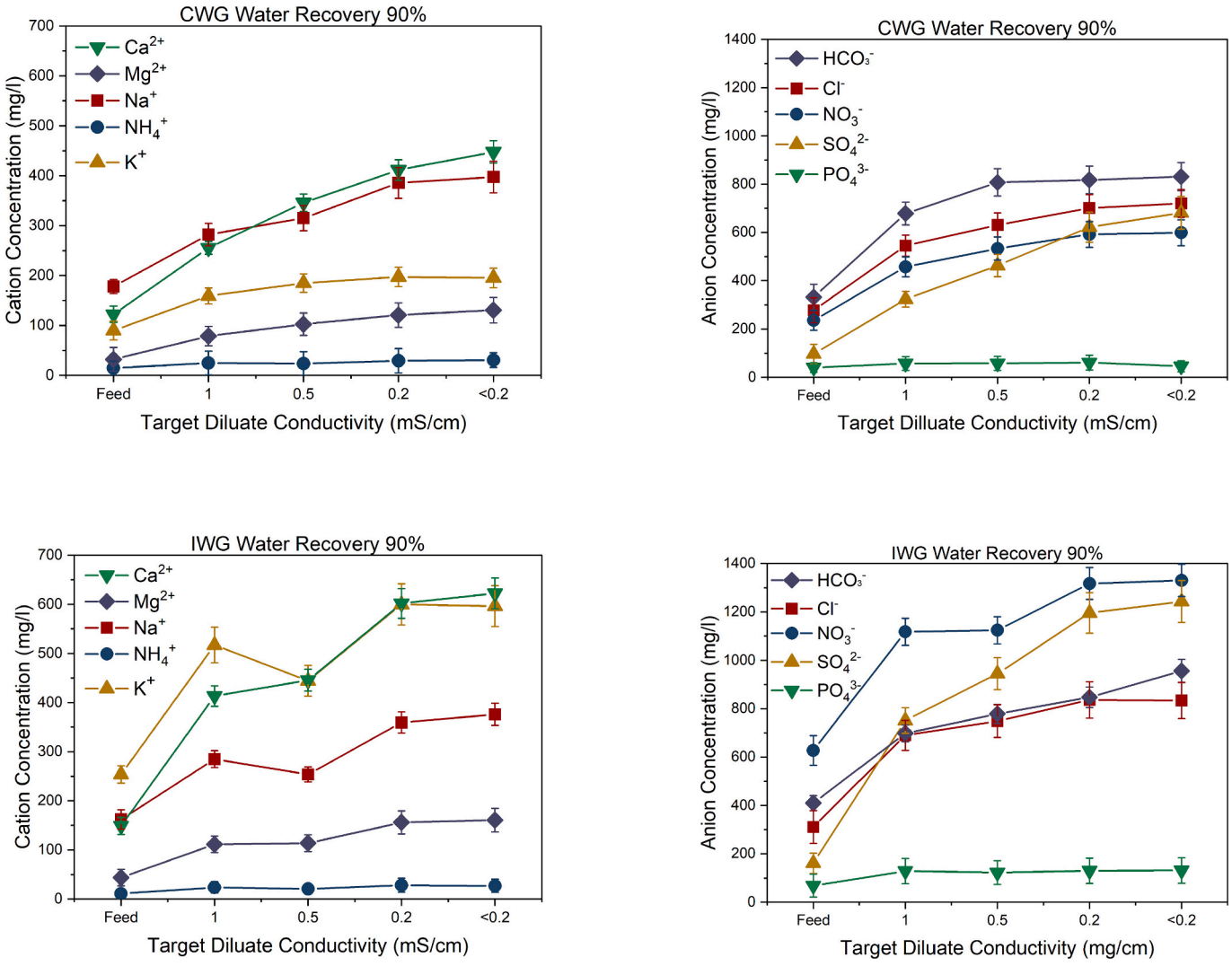

Fig. 8. Cation and anion concentrate composition for CGW and IGW composition at 90 % water recovery.

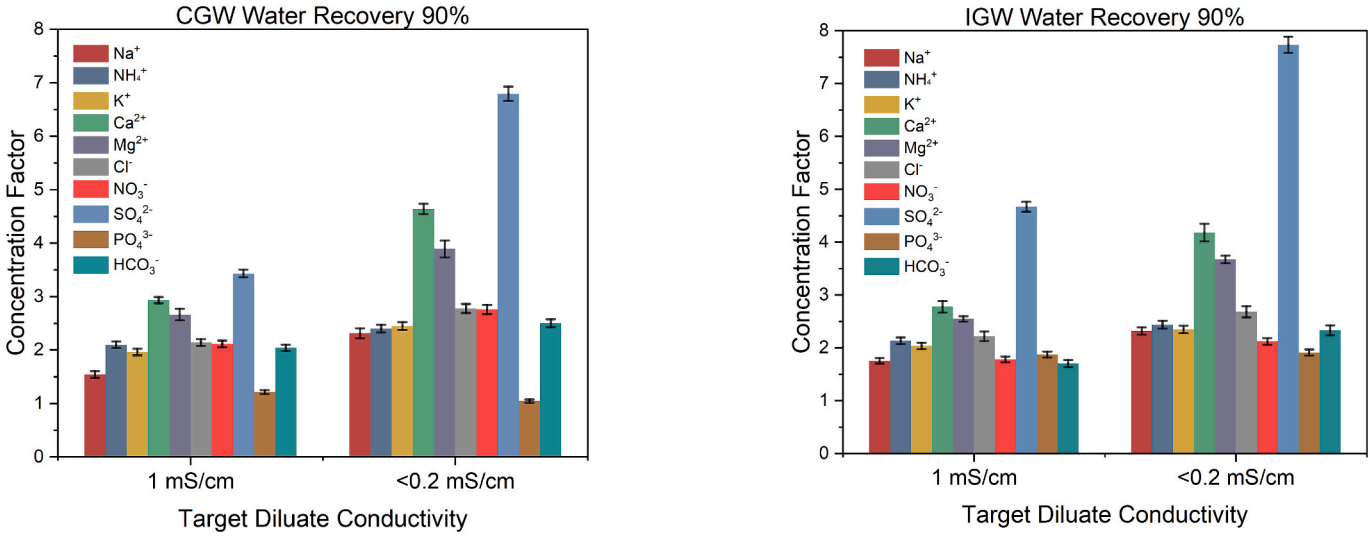

Fig. 9. Concentration factors for cations and anions for the CGW and IGW at 90 % water recovery.

to evaluate the impact of scaling and fouling on the overall process performance.

3.4. Capacitive electrodialysis (CED) energy consumption and comparison with reverse osmosis (RO) model

3.4.1. CED energy consumption

In this study, we determined specific energy consumption (SEC) of the CED system for varying greenhouse wastewater compositions IWG, CWG, and RCGW (Table 2), based on the optimized parameters previously determined; 5.12 cm/s and the 2-stage stack configuration, over 60–90 % water recoveries (membrane productivity of 4.5 L m^{-2} h^{-1}). For the highest irrigation water quality target (diluate conductivities <0.2 mS/cm), the stack SEC (stack) estimated was 0.09–0.14 kWh/m^3, with the highest SECs for CGW, RCGW, and IGW being 0.09, 0.11, and 0.14 kWh/m^3 respectively, at 90 % water recovery. Fig. 10a graphically represents the SECs obtained for CWG as a function of water recovery and targeted diluate conductivities. Detailed calculation for all compositions is provided in the supplementary information. The SEC tended to slightly decrease from 60 to 70 % water recovery and then stabilized from 80 to 90 %, particularly for IWG with higher initial feed composition. Apart from the stack, the pumping energy consumption was also considered. [17,84]. The pump's SEC (SECp) for the three wastewater types was calculated to be between 0.043 and 0.120 KWh/m^3, based on a pressure drop of 0.35–0.7 bar and 80 % efficiency. Total energy consumption (SEC stack and SEC Pump), excluding pre-treatment, post-treatment, and losses, was estimated to be 0.14–0.24 kWh/m^3 for the three feed compositions, with TDS ranging between 1200 and 2000 mg/L (Fig. 10b).

On average, the stack SEC was 12 % higher at water recovery of 90 % compared to 60 %. This can potentially be attributed to a higher concentration gradient difference between the dilute and concentrate, leading to more energy consumption. Furthermore, the total SEC is not significantly impacted by the energy required for pumping, attributed to the low hydraulic pressure and minimal pressure drop in the system. In literature, reported SEC values (without pumping) for electrodialysis-based systems range from 0.29 to 2.5 kWh/m^3 and from 2.64 to 7 kWh/m^3 for desalination, for TDS <3000 mg/L, and TDS >3000 mg/L, respectively [41,42,85–87]. For RO, in literature, reported SEC range from 0.36 to 5kWh/m^3, for TDS ranging from 2000 to 10,000 mg/L [86,88,89]. It should be noted that for an absolute comparison in terms of energy consumption the same metrics (feed TDS, salt removal, water recovery, membrane productivity) are important, however, this varies in literature. Comparatively, this study showcased a lower SEC for treating

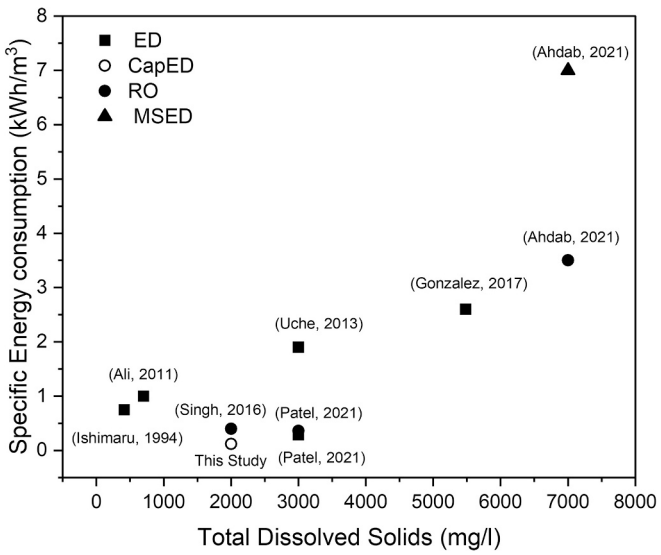

Fig. 11. Comparative analysis of specific energy consumption (SEC) in KWh/m^3 for the current study against existing literature. This figure illustrates the SEC values obtained in this study, juxtaposed with data from previous studies (Total Dissolved Solids (TDS) feed range from 200 to 7000 mg/L).

greenhouse wastewater, with the highest value recorded at 0.14 kWh/m^3, in contrast to the minimum values reported for ED and RO processes (0.29 kWh/m^3 for ED and 0.36 kWh/m^3 for RO), for similar TDS feeds (Fig. 11). This can be explained as, in general, for a given case, ED consumes energy in a range of 1–11 kWh/m^3 whereas capacitive technologies such as CDI and MCDI require energy inputs ranging from 0.1 to 1 kWh/m^3 [90–92]. The improvement in efficiency was likely due to the presence of IEMs near the electrodes mitigating co-ion effects and the strategic design of the CED cell, which allowed energy stored during charging to be used directly for desalination during discharging [48,93]. Furthermore, for CED losses at the electrodes would be lower due to absence of electrode reaction, reducing the overpotential (typically 1-2 V, based on electrode material) [94,95]. This demonstrates that CED is characterized by its low energy consumption for desalination, suggesting it could become a highly energy-efficient process. [48]. Furthermore, low energy consumption in this work's CED system, as compared to the reported values, could be attributed to the sector-targeted investigation and scale of the setups. While most existing studies are based on theoretical calculations or lab-scale experiments, our

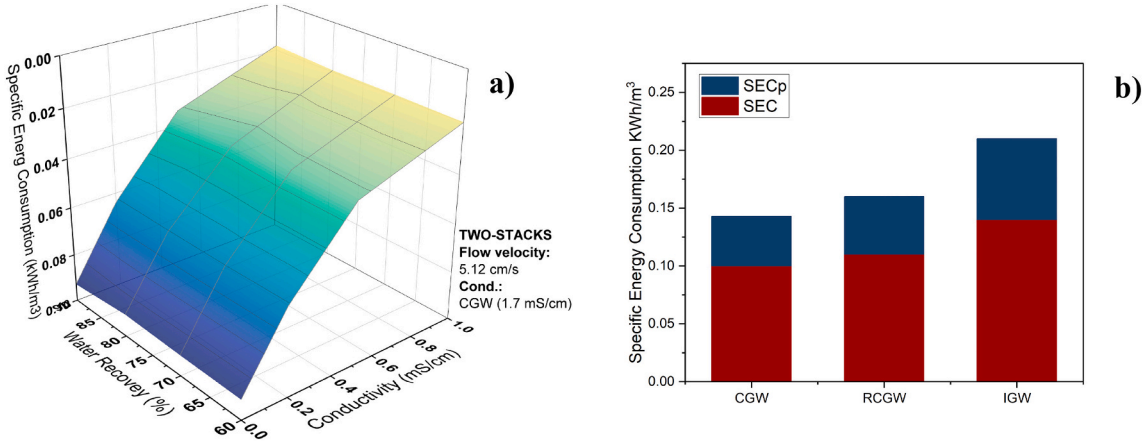

Fig. 10. a) Specific energy consumption (SEC) in KWh/m^3 for desalinating greenhouse wastewater (CGW feed composition (EC 1.7 mS/cm)) using CED. The color gradient from light green to dark blue represents an increase in SEC corresponding to target conductivities (1 to <0.2 mS/cm), achieved over water recoveries of 60–90 %. b) Total energy consumption (SEC stack and SEC Pump) for all compositions and 90 % water recovery. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

investigation provides pilot-scale experimental data with real feed water, offering a more realistic approximation for full-scale applications in the greenhouse horticulture sector. It should be considered that for full scale applications in this sector, it is suggested to combine CED with additional treatment technologies such as activated carbon to remove crop protection agents and disinfection (e.g., with UV) before storage to ensure the water for reuse is free of pesticides and plant pathogens.

3.4.2. *Comparison with a modeled Reverse Osmosis (RO) system for treating greenhouse wastewater*

To evaluate the performance of CED against RO, specifically for treating greenhouse wastewater under comparable conditions, we modeled a conventional RO system using the WAVE software (version 1.82, Dupont), without an energy recovery device. Fig. 12 depicts the comparative trends in SEC, diluate, and concentrate total TDS between CED and RO for desalinating greenhouse wastewater, with the CGW feed composition and target diluate conductivities of 1 mS/cm and 0.5 mS/cm (Table 2).

For RO, the model predicted an SEC of 0.8 kWh/m^3 at 50 % water recovery, decreasing to 0.56 kWh/m^3 at 70 % and plateauing at 90 %, in contrast to the substantially lower SEC determined previously for CED in this study (section 3.4). Notably, CED showed a modest 3.71 % increase in SEC when water recovery rose from 60 % to 90 %, whereas RO experienced a 14.29 % decrease in SEC with higher water recoveries, amounting to an overall 18 % decrease in SEC compared to CED. This difference is primarily due to CED's partial desalination approach, unlike RO's complete desalination. Previous studies have corroborated the energy efficiency of ED compared to RO, particularly at lower feed salinities [41,96]. Compared to CED, RO generated lower permeate TDS for recoveries between 50 and 90 %, with a slight decrease from increasing water recovery. The performance of both technologies is much closer for the concentrate, with RO showing higher concentration potential than CED and the gap widening for recoveries closer to 90 %. The CED process generated less and potentially more tunable

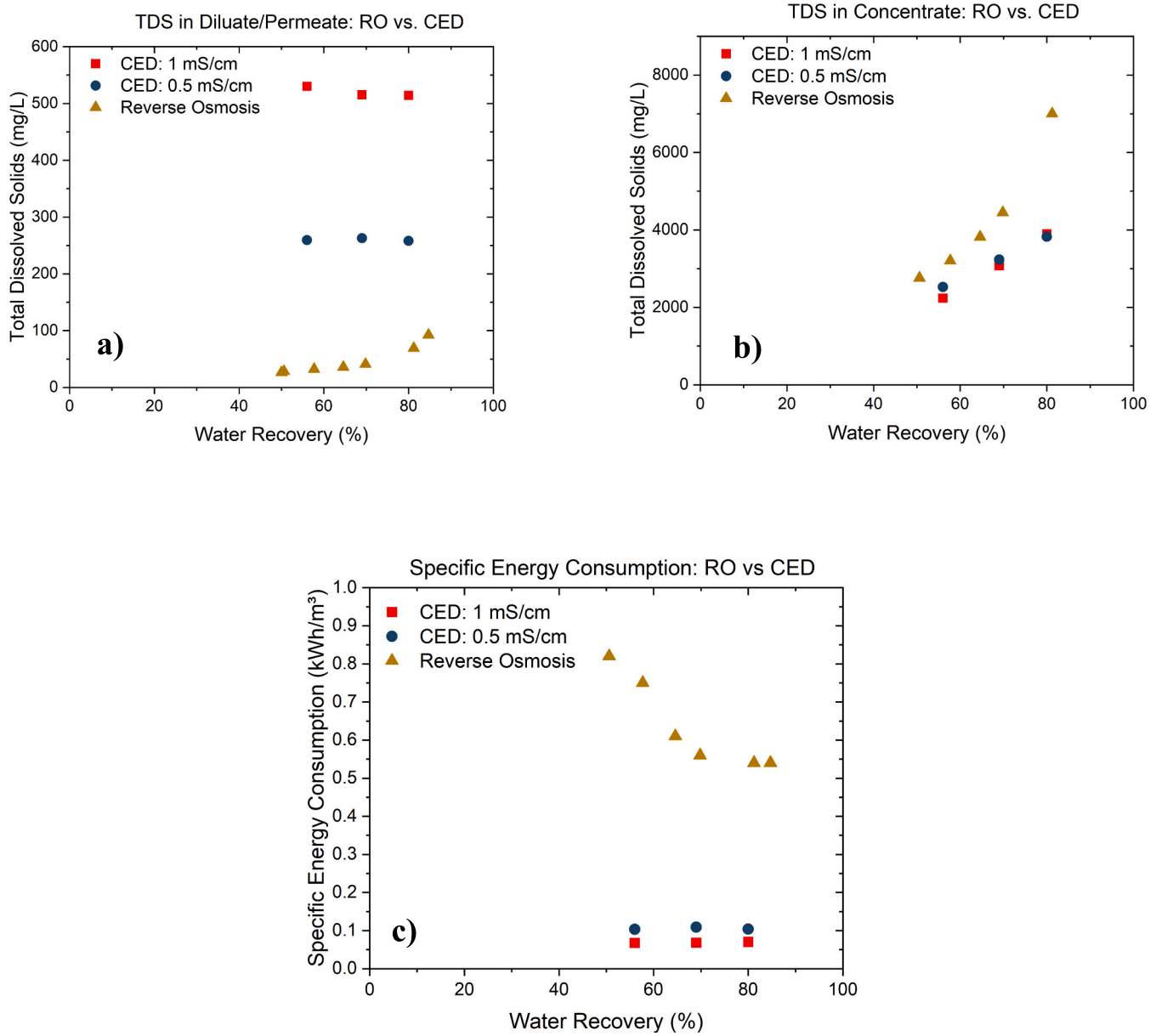

Fig. 12. Comparative evaluation of capacitive electrodialysis (CED) and reverse osmosis (RO) Technologies for a) ion removal performance, b) concentrate generated (TDS), and c) estimated SEC. CGW feed composition (EC 1.7 mS/cm) and cross-flow velocity of 5.12 cm/s considered as operating parameters for both technologies.

concentrate than RO.

4. Conclusions

There is a growing need for efficient technologies for decentralized water and resource recovery for crop production. This study assessed the feasibility of capacitive electrodialysis (CED) for reclaiming irrigation water and recovering nutrients from greenhouse wastewater at pilot scale from both individual and collective greenhouse wastewater. Key findings include;

- Optimal CED Operation: Achieving target diluate conductivities (1- < 0.2 mS/cm) at 60–90 % water recoveries was feasible with applied voltages of 6-16 V. However, voltages beyond 12 V and 80 % water recovery showed diminishing returns in ion removal efficiency, indicating energy inefficiency due to back diffusion or electrode polarization. The most effective ion removal was observed at a cross-flow velocity of 5.12 cm/s and with a 2-stage stack configuration. Furthermore, higher feed concentrations (2.5 mS/cm conductivity), from the range of greenhouse wastewater tested, showed improved ion removal.
- Diluate Ion Removal Efficiency: The study successfully achieved the highest target irrigation water quality across all feeds (conductivity 1- < 0.2 mS/cm, Na^+ and Cl^- < 0.1 mmol/L) with ions exhibiting variable removal efficiencies. Specifically, Na^+ removal was less efficient compared to Ca^{2+} and Mg^{2+} (86 % ± 4 %, 97 % ± 2 %, and 98 % ± 3 % for diluate quality <0.2 mS/cm, respectively), which was significantly affected by increasing voltage and water recovery.
- Nutrient Recovery: The CED process facilitated the concentration of valuable ions in the concentrate, offering potential for nutrient recovery as fertilizers. The highest concentration factors with collective (CGW) and individual (IGW) greenhouse wastewater feed were 2.4 and 2.3 for K^+, 3.8 and 3.6 for $Mg^{2+,}$ and 4.6 and 4.1 for Ca^{2+}, followed by 2.7 and 2.1 for NO_3^-, 6.7 and 7.7 for SO_4^{2-}, 1 and 1.9 for PO_4^{3-} at 90 % water recoveries. Notably, divalent ions displayed higher concentration factors compared to monovalent ions.
- Energy Efficiency: The total specific energy consumption (SEC) of the CED system ranged between 0.14 and 0.24 kWh/m^3 across different feed compositions. With optimal CED operating conditions, this was 4-fold lower than the modeled RO system, and significantly lower than reported ED and RO studies. While RO systems achieve lower conductivity in the diluate and higher concentrate, CED offers a superior energy-efficient alternative.

In conclusion, CED emerges as a promising alternative to traditional desalination techniques like RO, especially for producing fit-for-use irrigation water and recovering nutrients. Its advantages in terms of energy efficiency and tunable ion removal position CED as a sustainable solution for water and resource recovery in greenhouse horticulture.

Author agreement statement

We declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. We confirm that the manuscript has been read and approved by all named authors and that there are no other people who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us. We understand that the Corresponding Author is the sole contact for the Editorial process. He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

CRediT authorship contribution statement

Tavishi Guleria: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Joep van den Broeke:** Writing – review & editing, Supervision, Project administration. **Ides Platteau:** Investigation, Formal analysis, Data curation. **Timon Rijnaarts:** Writing – review & editing, Supervision. **Abdulsalam Alhadidi:** Writing – review & editing, Resources. **Leonardo Gutierrez:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Emile Cornelissen:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2024.117669.

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